

A Dinuclear Cd(II) Cluster-based Coordination Polymer: Synthesis, Structure and Luminescence Property

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ABSTRACT One two-dimensional coordination polymer with a formula of $\{[\text{Cd}(\text{L})(\text{imidazole})(\text{H}_2\text{O})](\text{H}_2\text{O})\}_n$ (**1**) was obtained by the synthetic reactions in aqueous solution using a newly synthesized H_2L (H_2L = methyl-3-hydroxy-5-carboxy-2-thiophenecarboxylate) ligand. Compound **1** crystallizes in monoclinic system, space group $C2/c$ with $a = 18.3176(11)$, $b = 8.5366(9)$, $c = 8.4152(5)$ Å, $\beta = 101.789(6)$ °, $V = 2797.1(3)$ Å³, $D_c = 1.979$ g/cm³, $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_7\text{SCd}$, $M_r = 416.68$, $F(000) = 1648$, $\mu = 1.745$ mm⁻¹, $F(000) = 1648$, the final $R = 0.0323$ and $wR = 0.0604$ for 2604 observed reflections with $I > 2\sigma(I)$. Structure analyses reveal that the compound is constructed by dinuclear Cd(II) clusters bridged by two hydroxyl oxygens of L^{2-} anions, which features a two-dimensional network with 4-connected *sql* topology. Furthermore, the compound exhibits high thermal stability and intense fluorescent emission, and could be explored for potential luminescent materials.

Keywords: methyl-3-hydroxy-5-carboxy-2-thiophenecarboxylate; topology; luminescence property;

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1 INTRODUCTION

Recently, a great deal of attention has been focused on the assembly of coordination polymers (CPs) owing to their various intriguing constructions and potential applications as functional materials^[1-6]. In order to synthesize novel CPs, the rational design and assembly of metal ions or metal clusters with diverse multifunctional bridging linkers are sensible and effective^[7-10]. Among them, organic bridging linkers containing multidentate carboxylic acids have been fully used as building blocks in crystal engineering. However, building blocks based on thiophenedicarboxylic acids for assembly are still rare. In recent years, our group and others have been involved in the synthesis of CPs constructed from various thiophenedicarboxylic acids, such as 2,5-thiophenedicarboxylic acid, 3,4-thiophenedicarboxylic acid, 2,3-thiophenedicarboxylic acid and 3-nitro-2,5-thiophenedicarboxylic acid, and many interesting CPs have been reported^[11-15].

In this regard, the methyl-3-hydroxy-5-carboxy-2-thiophenecarboxylate (H_2L) was selected as a precursor trying to construct CPs because the new thiophene-2,5-dicarboxylic acid derivative has multiple potential coordination sites involving carboxyl, hydroxyl and carbomethoxyl groups. In addition, the Cd(II) ion with larger ionic radius is able to tolerate various coordination numbers and geometries in crystal engineering. Encouraged by these findings above mentioned, we choose H_2L and imidazole mixed linkers to investigate its assembly with the Cd(II) ion. Fortunately, one two-dimensional CP constructed from dinuclear Cd(II) clusters was obtained. The compound with 4-connected *sql* topology is then characterized by infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA). Moreover, the luminescent property of the compound has also been investigated.

2 EXPERIMENTAL

All reagents and solvents were purchased commercially and used without further purification. The IR spectra were recorded as KBr pellets on a Nicolet Avatar-360 spectrometer in the range of 4000 to 400 cm^{-1} . Elemental analyses for C, H, and N were carried out on a Flash 2000 elemental analyzer. The TGA was carried out on a SDTQ600 thermogravimetric analyzer. A platinum pan was used for heating the sample with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under air atmosphere. Fluorescence measurements were recorded with a Hitachi F4500 fluorescence spectrophotometer.

2.1 Synthesis of the compound $\{[\text{Cd}(\text{L})(\text{imidazole})(\text{H}_2\text{O})](\text{H}_2\text{O})\}_n$ (1)

A mixture of H_2L (20.2 mg, 0.1 mmol), $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (26.7 mg, 0.1 mmol), imidazole (13.62 mg, 0.2 mmol), NaOH (2.00 mg, 0.05 mmol) and 4 mL deionized water was sealed in a 20 mL Pyrex glass tube and heated at 80 $^{\circ}\text{C}$ for 72 h, followed by cooling to room temperature at a rate of 5 $^{\circ}\text{C} \text{ h}^{-1}$. Block yellow crystals were collected (yield: 62% based on Cd). Elemental analysis calcd. (%) for $\text{C}_{10}\text{H}_{12}\text{CdN}_2\text{O}_7\text{S}$: C, 28.79; H, 2.88; N, 6.72. Found (%): C, 28.81; H, 2.89; N, 6.69. Selected IR peaks (KBr, cm^{-1}): 3517 (s), 3357 (m), 3296 (m), 2639 (m), 1593 (s), 1536 (s), 1464 (s), 1433 (s), 1375 (s), 1342 (s), 1166 (m), 920 (m), 836 (m), 755 (m), 734 (m), 715 (m), 686 (m).

2.2 X-ray structure determination

A suitable crystal of compound **1** was mounted on a glass fiber using a viscous hydrocarbon oil to coat the crystal. Crystal structure determination diffraction data of compound **1** were collected on an Oxford Diffraction SuperNova Eos2 diffractometer equipped with a graphite-monochromatic $\text{MoK}\alpha$ radiation at 293(2) K. The data were collected and processed using the CrysAlisPro software, and the structures were solved using the Olex2 program as an interface together with the SHELXS and SHELXL programs, in order to solve and refine the structure, respectively^[16–18]. Heavy atoms were refined anisotropically. Except that the aqueous

hydrogen atoms were determined from difference Fourier maps and fixed the distances of O–H (0.85 Å), the other hydrogen atoms were added in the riding model without refinement. Selected bond distances (Å) and bond angles (°) of **1** are summarized in Table 1. The final $R = 0.0323$ and $wR = 0.0604$ for 2604 observed reflections with $I > 2\sigma(I)$ and $R = 0.0418$ and $wR = 0.0634$ for all data. $(\Delta\rho)_{\max} = 0.641$, $(\Delta\rho)_{\min} = -0.496$ e/Å³ and $S = 1.061$.

3 RESULTS AND DISCUSSION

3.1 Crystal structure

Complex **1** was obtained as block yellow crystalline materials by the reaction of H₂L and cadmium acetate with imidazole in aqueous medium. It should be noted that the weak basic pH values in the starting reaction solutions are essential to successfully prepare the compound. Attempts to synthesize **1** in an acidic or neutral pH value failed. The reasons may be because the weak basic environments could facilitate H₂L deprotonation and make it easy to coordinate with Cd²⁺ ion, which was also consistent with the single-crystal X-ray analysis.

Complex **1** crystallizes in monoclinic space group $C2/c$, and there exist one Cd^{2+} ion, one L^{2-} anion, one imidazole ligand, one coordinated water molecule and one lattice water molecule in the asymmetric unit (Fig. 1). The Cd^{2+} ion shows a distorted octahedral geometry, coordinated by four oxygen atoms from three L^{2-} anions, one imidazole nitrogen atom from one terminal imidazole ligand and one coordinated water molecule.

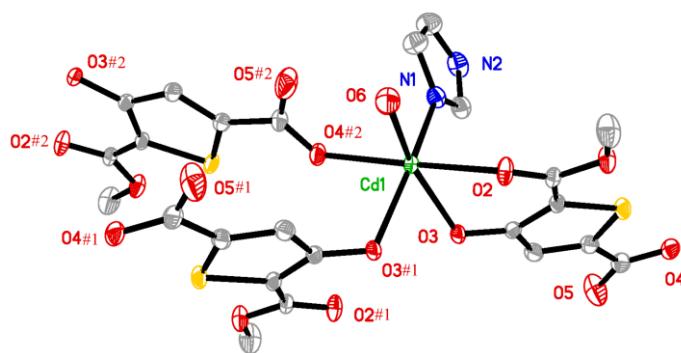


Fig. 1. Coordination environment of the Cd(II) center. Hydrogen atoms are omitted for clarity.

Symmetry codes: #1: $1.5 - x, 0.5 - y, 2 - z$; #2: $1.5 - x, y - 0.5, 1.5 - z$

The bond length of Cd–N is 2.263(3) Å, while the Cd–O bond lengths range from 2.265(2) to 2.379(2) Å, which are in the normal range^[19, 20]. The O–Cd–O angles range between 77.34(9) and 171.31(9)°, and the O–Cd–N angles can be found in the 86.16(11)–161.94(11) °region (Table 2).

In **1**, each L^{2-} anion in a tridentate $\mu_3\text{-}(\eta^2\text{-})(\eta^1\text{-})(\eta^1\text{-})$ bridging mode links adjacent Cd^{2+} ions, thereby generating a 2D layer structure running parallel to the bc plane, which is further decorated by the terminal imidazole ligand (Fig. 2a and Fig. 2b). In **1**, a pair of Cd^{2+} ions is bridged by a pair of hydroxyl oxygen atoms to give a dinuclear Cd_2O_2 cluster with a shorter $\text{Cd} \cdots \text{Cd}$ separation of 3.5500 Å. In topology, such a Cd_2O_2 cluster can be viewed as a 4-connected node to link four other equivalent ones through four L^{2-} anions, thus forming a 4-connected *sql*-type network with $4^4 6^2$ topology (Fig. 2c). Moreover, such 2D layers are extended into an overall three-dimensional (3D) network by intermolecular $\text{O}-\text{H} \cdots \text{O}$ interactions between the lattice water ($\text{O}(7)$) and oxygen atoms of L^{2-} /or coordinated water molecule ($\text{O}(7)\text{-H}(3\text{W}) \cdots \text{O}(5)$, $\text{O}(7)\text{-H}(3\text{W}) \cdots \text{O}(6)$ and $\text{O}(7)\text{-H}(4\text{W}) \cdots \text{O}(5)$; Table 2 lists the detailed hydrogen-bonding geometry, as shown in Fig. 2d.

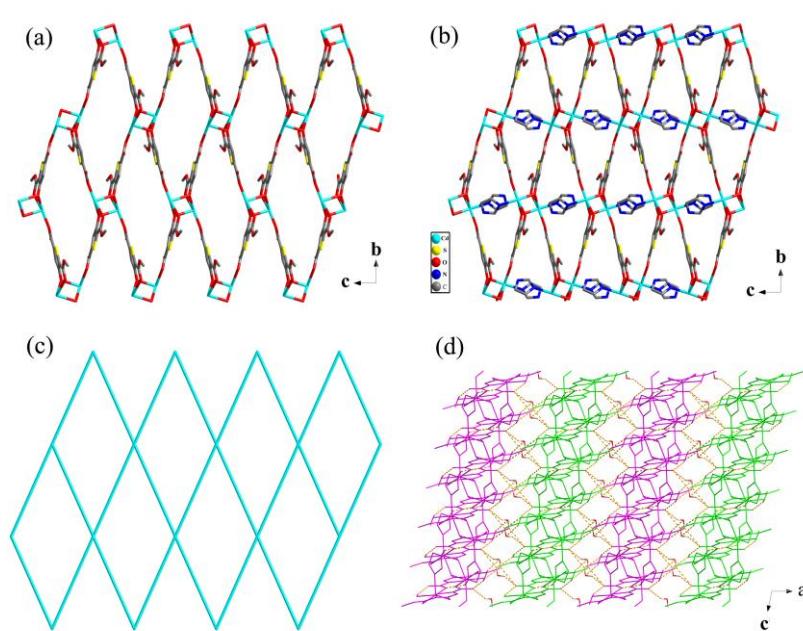


Fig. 2. (a) 2D layer structure in **1**. (b) 2D layer decorated by imidazole ligand.

(c) Schematic representation of the 4-connected *sql* topology. (d) View of the 3D hydrogen-bonded network

Table 2. Hydrogen Bonds for Compound **1**

D-H \cdots A	d(D-H)	d(H \cdots A)	d(D \cdots A)	\angle (DHA)

O(6)–H(2W) .. O(5) ^{#2}	0.85	1.83	2.582(4)	146.2
N(2)–H(2) .. O(4) ^{#3}	0.86	2.20	2.910(5)	140.2
O(6)–H(1W) .. O(7) ^{#4}	0.85	2.53	3.113(10)	126.4
O(7)–H(3W) .. O(5) ^{#5}	0.85	2.57	3.260(9)	138.5
O(7)–H(3W) .. O(6) ^{#6}	0.85	2.58	3.113(10)	121.9
O(7)–H(4W) .. O(5) ^{#7}	0.85	2.28	3.063(8)	153.3

Symmetry codes for compound **1**: #2: $1.5 - x, y - 0.5, 1.5 - z$; #3: $x, 1 - y, z - 0.5$; #4: $x, y, 1+z$; #5: $x - 0.5, y - 0.5, z - 1$; #6: $x, y, z - 1$; #7: $1.5 - x, 0.5 - y, 1 - z$

In addition, this structure also contains intramolecular hydrogen-bonding involving carbonyl and terminal imidazole moieties (N(2)–H(2) .. O(4) and O(6)–H(2W) .. O(5); see Table 2 for detailed hydrogen-bonding geometry), which further promote the stability and integrity of the 3D supramolecular network.

3.2 IR spectrum and thermal study

In compound **1**, IR spectra exhibit strong absorption centered at $3517 \sim 2639 \text{ cm}^{-1}$, corresponding to the N–H/O–H stretching vibration of imidazole ligand or water molecule. In the characteristic stretching vibrations of the carboxylate groups, the absorbance peaks in the $1593 \sim 1536$ and $1342 \sim 1464 \text{ cm}^{-1}$ ranges are attributed to the asymmetric and symmetric stretching, respectively. The absence of absorption peak at the $1690 \sim 1730 \text{ cm}^{-1}$ region suggests the complete deprotonation of carboxylate groups in the H₂L ligand. The thermal stability of **1** was investigated on the crystalline sample at a heating rate of $10 \text{ }^{\circ}\text{C min}^{-1}$ under air atmosphere. As seen in Fig. 3, a two-step weight loss was observed. The first step of weight loss (observed: 7.62%) between 57 and $117 \text{ }^{\circ}\text{C}$ was attributable to the release of two water molecules (expected: 7.68%). A steady platform appears in the temperature region of $117 \sim 234 \text{ }^{\circ}\text{C}$. Further heating gives rise to the continuous weight loss due to the decomposition of organic moieties.

3.3 Luminescent property

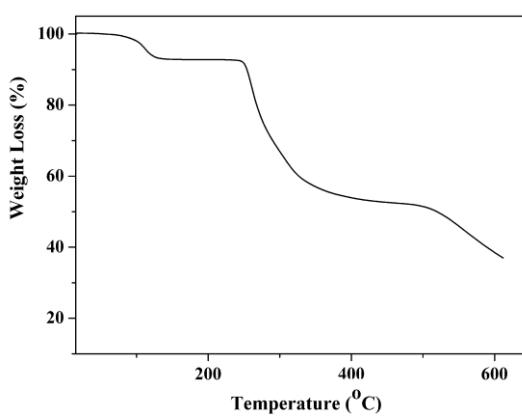
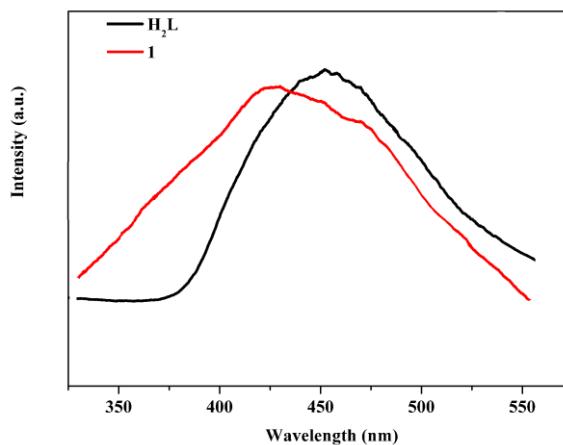


Fig. 3. TGA curve for **1****Fig. 4.** Solid-state emission spectra of **1** and the free H_2L ligand measured at room temperature

Since compound **1** is stable in air and insoluble in water or most organic solvents, the luminescent properties of the crystalline sample of **1** and the H_2L ligand were investigated in the solid state at room temperature. As seen in Fig. 4, complex **1** exhibits fluorescent emission with the maxima at 430 nm ($\lambda_{\text{ex}} = 272$ nm). Such fluorescence behavior may be attributed to the intraligand transition of coordinated L^{2-} anions since similar emission at 452 nm ($\lambda_{\text{ex}} = 276$ nm) was observed for the free H_2L ligand. The blue-shifted emission of **1** was caused by the coordination of L^{2-} anions to the metal centers^[21].

4 CONCLUSION

In the present study, a Cd(II) coordination polymer containing dinuclear Cd(II) clusters was successfully constructed and characterized. The single-crystal X-ray diffraction shows that the L^{2-} anion takes a bidentate $\mu_2\text{-}(\eta^1,\eta^1)\text{-}(\eta^1)$ bridging mode to link adjacent Cd(II) ions, forming a 2D layer structure with 4-connected *sql* topology, which are further connected by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding interactions to form a 3D

supramolecular framework. Moreover, the compound exhibits high thermal stability and intense fluorescent emission, and can be explored for potential luminescent materials.

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Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Dist.	Bond	Dist.	Bond	Dist.
Cd(1)–N(1)	2.263(3)	Cd(1)–O(2)	2.379(3)	Cd(1)–O(3)	2.265(2)
Cd(1)–O(6)	2.290(3)	Cd(1)–O(3)#1	2.282(2)	Cd(1)–O(4)#2	2.328(2)
Angle	(°)	Angle	(°)	Angle	(°)
N(1)–Cd(1)–O(6)	99.44(12)	O(3)–Cd(1)–O(2)	77.45(9)	O(3)#1–Cd(1)–O(2)	93.26(9)
O(3)–Cd(1)–O(3)#1	77.34(9)	O(3)#1–Cd(1)–O(4)#2	83.73(9)	O(3)–Cd(1)–O(4)#2	109.68(9)
O(3)–Cd(1)–O(6)	157.11(10)	O(3)#1–Cd(1)–O(6)	95.65(10)	O(4)#2–Cd(1)–O(2)	171.31(9)
O(6)–Cd(1)–O(2)	81.29(10)	O(6)–Cd(1)–O(4)#2	90.88(11)	N(1)–Cd(1)–O(2)	98.76(11)
N(1)–Cd(1)–O(3)	92.11(11)	N(1)–Cd(1)–O(3) #1	161.94(11)	N(1)–Cd(1)–O(4) #2	86.16(11)

Symmetry transformation: #1: $1.5 - x, 0.5 - y, 2 - z$; #2: $1.5 - x, y - 0.5, 1.5 - z$

A Dinuclear Cd(II) Cluster-based Coordination Polymer: Synthesis, Structure and Luminescence Property

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One 2D dinuclear Cd(II) cluster-based coordination polymer with 4-connected *sql* topology was obtained using a new methyl-3-hydroxy-5-carboxy-2-thiophenecarboxylate and imidazole mixed ligand.

